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Amides in One Pot from Carboxylic Acids and Amines via Sulfinylamides

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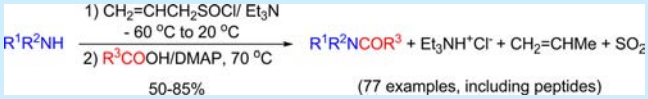
Supporting Information

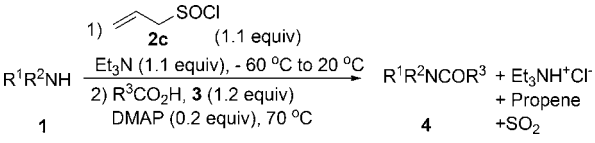
ABSTRACT: An efficient method has been developed for the direct amidification of carboxylic acids via sulfinylamides preformed in situ by the reaction of pure amines with prop-2-ene-1-sulfinyl chloride. The method can be applied to aliphatic acids, including pivalic acid, aromatic acids, and primary and secondary amines. It is compatible with acids bearing unprotected alcohol, phenol, and ketone moieties and applicable to the synthesis of peptides. It does not induce their α-epimerization.



Amide formation from carboxylic acids and amines is a fundamental reaction in organic, biological, medicinal, polymer, and material chemistry for which a great amount of research is still pursued.[1] Most methods rely upon nucleophilic addition of the free amines onto an activated acyl compound derived from the carboxylic acid.[2] We report here a new approach that relies on activation of amines **1** in the form of sulfinyl amides.[3,4]

Under high temperature microwave conditions, isonitriles react with carboxylic acids to give carboxamides.[5] Thioacids have been reacted with isonitriles,[6] isocyanates,[7] azides,[8] and amides.[9] The main challenge is to find mild reaction conditions that avoid α-epimerization of the carboxylic acids and of the corresponding carboxamides and that tolerate other unprotected functions or functions protected adequately for further use of the carboxamides in fine synthesis. This is the case with our new method (Scheme 1), as neither a strong base nor acid

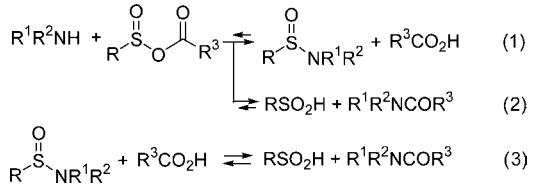
Scheme 1. General Method of One-Pot Direct Amidification of Carboxylic Acid



is required. Furthermore, purification of the carboxamides is facilitated by the fact that the coproducts of the reaction are $Et_3NH^+Cl^-$ and volatile propene and SO_2, and only a 20% excess of acid is used.

Recently we reported that mixed anhydrides of sulfinyl and carboxylic acids (sulfinyl carboxylates: RS(=O)−O−COR^3) react at 20 °C with all kinds of nucleophiles including primary and secondary amines at sulfur exclusively in the reaction (Scheme 2, eq 1), unless steric hindrance (R: CH_2═CH−CMe_2) permits the addition to the carbonyl group to compete, and also with amines, to generate the corresponding carboxamides as in the reaction (Scheme 2, eq 2).[2] The related

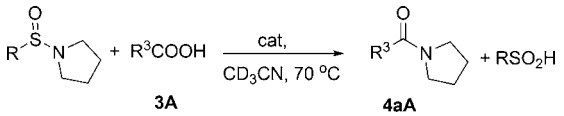
Scheme 2. Activation of Carboxylic Acids and Amines by the Sulfinyl Group



reaction (Scheme 2, eq 3) should equilibrate sulfinylamides and carboxylic acids with carboxamides and sulfinyl acids. It could be a useful route for the direct amidification of carboxylic acids, as sulfinyl amides are readily available.[10]

Our exploratory studies started with the reaction of *p*-toluenesulfinylamide[11] **5aa** and 3-phenylpropionic acid **3A** (Scheme 3). Using a 0.1 M solution of **3A** and **5aa** in MeCN a

Scheme 3. Sulfinyl-Carbonyl Exchange Reactions



5aa, R = *p*-Tol
5ab, R = Me
5ac, R = CH_2=CH-CH_2
5ad, R = Me_2C=CH-CH_2
5ae, R = *p*-$Me_2NC_6H_4$
5af, R = *p*-Me-*o*-$Me_2NC_6H_3$

6a
6b
6c
6d
6e
6f

slow reaction was observed at 70 °C giving the expected carboxamide **4aA** and *p*-toluenesulfinic acid **6a**. DMAP (4-dimethylaminopyridine) accelerated the reaction. With 0.2 equiv of DMAP at 70 °C a half-life of 8 h was evaluated by ^{1}H NMR. The rate enhancement induced by 0.2 equiv of DMAP was *ca.* 5-fold. As we thought that the addition of **3A** to the

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sulfinyl amide could be accelerated by increasing its electrophilicity, we explored the reaction of pyrrolidine *p*-nitrobenzenesulfinyl amide[12] with **3A**. To our surprise no trace of carboxamide **4aA** did form after prolonged heating to 70 °C, in the absence or in the presence of 1 equiv of DMAP. Similarly, no reaction could be observed under the same reaction conditions with pyrrolidine trifluoromethanesulfinyl amide[13] and pyrrolidine isobutyronitrilesulfinyl amide.[14] On heating carboxamide **4aA** to 70 °C with CF_3SO_2H, with or without DMAP, no sulfinyl/carbonyl exchange could be seen. The reactions of **3A** with methanesulfinyl amide **5ab**[15] and prop-2-enesulfinyl amide **5ac**[16] (0.2 equiv of DMAP as the catalyst) at 70 °C were faster than with *p*-toluenesulfinyl amide **5aa** under the same conditions and gave carboxamide **4aA**. Half-lives of 4 and 1 h were evaluated for reactions **3A** + **5ab** and **3A** + **5ac**, respectively. The two latter reactions are *ca.* twice and 8 times, respectively, as fast as reaction **3A** + **5aa**. Upon prolonged heating of **3A** with **5ab** full conversion of **5ab** was reached after 6 h and **4aA** was isolated in 74% yield only.

After 1 equiv of Et_3N was added to neutralize $MeSO_2H$ **6b** formed as the coproduct, the yield of pure **4aA** increased to 90%. In a parallel experiment we demonstrated that $MeSO_2H$ induces the slow decomposition of **5ab**. With sulfinyl amide **5ac** no base is required to neutralize the sulfinic acid formed, as the latter (prop-2-enesulfinic acid, **6c**) undergoes a quick retro-ene reaction at 70 °C with formation of volatile propene and SO_2.[17] When using a 20% excess of the carboxylic acid **3A** and 20 mol % of DMAP, the medium never becomes basic or acidic as verified for aliquots mixed with water (pH 4.5 to 3.5). Most importantly, the amidification yield was the highest for reaction **3A** + **5ac**. As electron-poor sulfinylamides failed to produce carboxamides, we explored the reaction of **3A** with electron-rich sulfinylamides **5ad**, **5ae**, and **5af**. They all produced carboxamide **4aA** but more slowly than reaction **3A** + **5ac**. Carboxylic acids **3B**−**3T** were then reacted with **5ac**. The results are summarized in Table 1.

Except for 4-*p*-dimethylaminobenzoic acid all the reactions produced the expected carboxamides (Table 1). Linear and α-monobranched aliphatic carboxylic acids reacted the quickest and led to good yields of the corresponding amides. Pivalic acid **3I** reacted more slowly and gave amide **4aI** after 32 h at 70 °C in an acceptable yield of 57%. Benzoic acids reacted more slowly than cyclopentanecarboxylic acid **3S**. Better yields were obtained with electron-poor benzoic acid derivatives **3J**, **3K** than with electron-rich ones **3M**, **3N**. However, *o*-hydroxybenzoic acid **3L** led to a good yield of **4aL**. Most interesting is the observation that our reaction conditions are compatible with the presence of unprotected alcohol, phenol, and ketone moieties. With (*S*)-phenylsuccinic acid **3T** a 1:2 mixture of monoamides **4aT** + **4aT′** formed (^{1}H NMR). The same occurred when mixing pyrrolidine **1a** (1.0 equiv) with phenylsuccinic anhydride.

We then generated propene-2-sulfinyl amides from piperine **1b**, benzyl amine **1c**, aniline **1d**, (*S*)-1-methylbenzylamine **1e**, *tert*-butyl ester of L-valine **1f**, and L-proline **1g** and reacted them with a large variety of carboxylic acids **3** including N-protected α-amino acids. All the reactions produced the expected carboxamides in good yields (not shown). As we found that $Et_3NH^+Cl^-$ does not perturb the reactions of sulfinylamide **5ac** with acids **3**, we developed a one-pot, direct amidification of carboxylic acids. Our results are summarized in Table 2 (for more examples, see Supporting Information). The method is successful for primary and secondary amines. It did not work with indole which is sulfinylated at C3 with prop-2-enesulfinyl chloride **2c** (not shown).

Table 1. Amidification of Carboxylic Acids with Sulfinylamide 5ac[a]

R^3COOH, **3**	**4a**	time (h)	yield (%)
$PhCH_2CH_2CO_2H$, **3A**	**4aA**	6	94
$PhCH_2CO_2H$, **3B**	**4aB**	6	90
$PhCO_2H$, **3C**	**4aC**	12	88
$PhCOCH_2CH_2CO_2H$, **3D**	**4aD**	6	89
(*E*)-$PhCH{=}CHCO_2H$, **3E**	**4aE**	8	85
2-OH-$C_6H_4CH_2CO_2H$, **3F**	**4aF**	6	90
(*S*)-mandelic acid, **3G**	**4aG**	8	85
(*S*)-lactic acid, **3H**	**4aH**	8	75
t-Bu-CO_2H, **3I**	**4aI**	32	57
4-NO_2-$C_6H_4CO_2H$, **3J**	**4aJ**	10	77
4-CF_3-$C_6H_4CO_2H$, **3K**	**4aK**	8	73
2-OH-$C_6H_4CO_2H$, **3L**	**4aL**	8	78
4-CH_3O-$C_6H_4CO_2H$, **3M**	**4aM**	48	50
4-Me_2N-$C_6H_4CO_2H$, **3N**	**4aN**	48	0.
3-(3-pyridinyl)propionic acid, **3Ob**	**4aO**	6	83
(*E*)-3-(2-thienyl)acrylic acid, **3P**	**4aP**	10	81
Isobutyric acid, **3Q**	**4aQ**	6	82
n-Pent-CO_2H, **3R**	**4aR**	6	81
c-Pent-CO_2H, **3S**	**4aS**	6	82
(*S*)-phenylsuccinic acid, **3T**	**4aT**	3	76

[a]Conditions: **5ac** (0.75 M)/**3**/DMAP (1:1.2:0.2) in MeCN at 70 °C. Yield of amide **4** after workup. DMF (5−10% v/v) was added when the acid was not completely soluble in CD_3CN.

Using *tert*-butyl esters of L-valine **1f** and L-proline **1g** as amines and benzyl carbamates of glycine **3U**, L-proline **3V**, and L-valine **3W** as acids, the six protected dipeptides **4fU**, **4gU**, **4fV**, **4gV**, **4fW**, and **4gW** were obtained. The ^{1}H and ^{13}C NMR spectra of concentrated solutions of compounds **4eV**, **4eW**, **4fV**, **4fW**, **4gV**, and **4gW** (with two stereogenic centers) did not show any detectable α-epimerization (comparison with the spectra of amides made from racemic valine and proline). The 100 °C ^{1}H NMR spectra of **4eV** and **4eW** showed smaller signals for the methyl group of diastereomeric amides than the ^{13}C-satellites of the methyl signals of these compounds. In these two cases, if α-epimerization has occurred, it represents less than 0.5% (see Supporting Information).

The mechanism of the sulfinyl/carbonyl exchange disclosed here has not been established yet. It might involve the formation of the corresponding sulfinyl carboxylate intermediates **8** via addition of the carboxylic acids **3** to sulfinylamides **5** (Scheme 4). Then the liberated amines **1** add competitively to the sulfinyl (k_{SO}) and carbonyl group (k_{CO}), equilibrating back with **5** or producing amides **4**. This would explain why bulky aliphatic acids and electron-rich benzoic acids are producing amides more slowly. It explains also why sulfinyl amides derived from electron-poor sulfinyl acids such as 4-nitrobenzenesulfinic acid and triflic acid did not generate any carboxamide. In the absence of a carboxylic acid, with/without DMAP, external amines do not exchange with those of the sulfinylamides (70 °C, 12 h). However, they do exchange in the presence of a carboxylic acid. With/without DMAP, EtOH does not react with **5ac** (70 °C, 12 h). In the presence of 3-phenylpropionic acid **3A**, a mixture of ethyl sulfinic ester **9a** and amide **4aA** is obtained (70 °C, 3 h). EtOH competes with amine **1a** for the attack to the sulfinyl moiety. With *i*-PrOH no sulfinic ester is formed, only amide **4aA** is obtained. In contrast, when heating

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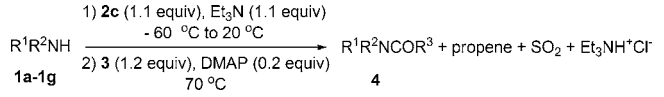
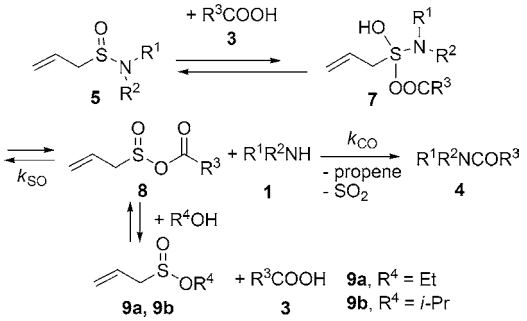
Table 2. One-Pot Amidification of Carboxylic Acids 3 with Amines 1[a]



R^3COOH, **3**	NH, **1a** 4 (yield)	NH, **1b** 4 (yield)	$BnNH_2$, **1c** 4 (yield)	$PhNH_2$, **1d** 4 (yield)	Ph(S)NH_2, **1e** 4 (yield)	H_2N(S)CO_2-*t*-Bu, **1f** 4 (yield)	N(S)CO_2-*t*-Bu, **1g** 4 (yield)
$PhCH_2CH_2CO_2H$, **3A**	**4aA** (80%)[b]	**4bA** (85%)[c]	**4cA** (80%)[e]	**4dA** (80%)[e]	**4eA** (80%)[e]	**4fA** (82%)[e]	**4gA** (82%)[f]
$PhCH_2CO_2H$, **3B**	**4aB** (81%)[b]	**4bB**: (84%)[c]	**4cB** (80%)[e]	**4dB** (82%)[e]	**4eB** (82%)[e]	**4fB** (83%)[e]	**4gB** (84%)[f]
$PhCO_2H$, **3C**	**4aC** (70%)[f]	**4bC** (73%)[f]	**4cC** (63%)[h]	**4dC** (60%)[h]	**4eC** (65%)[h]	**4fC** (61%)[i]	**4gC** (34%)[i]
$PhCOCH_2CH_2CO_2H$, **3D**	**4aD** (72%)[h]	**4bD** (75%)[c]	**4cD** (68%)[e]	**4dD** (63%)[e]	**4eD** (73%)[e]	**4fD** (68%)[e]	**4gD** (75%)[f]
(*E*)-$PhCH{=}CHCO_2H$, **3E**	**4aE** (71%)[d]	**4bE** (74%)[e]	**4cE** (67%)[h]	**4dE** (55%)[h]	**4eE** (69%)[g]	**4fE** (68%)[f]	**4gE** (65%)[f]
2-OH-$C_6H_4CH_2CO_2H$, **3F**	**4aF** (80%)[e]	**4bF** (83%)[d]	**4cF** (83%)[e]	**4dF** (82%)[e]	**4eF** (79%)[e]	**4fF** (77%)[e]	**4gF** (80%)[f]
(*S*)-Mandelic acid, **3G**	**4aG** (70%)[g]	**4bG** (75%)[e]	**4cG** (65%)[e]	**4dG** (63%)[e]	**4eG** (71%)[f]	**4fG** (67%)[f]	**4gG** (74%)[f]
(*S*)-Lactic acid, **3H**	**4aH** (74%)[e]	**4bH** (73%)[f]	**4cH** (70%)[e]	**4dH** (71%)[g]	**4eH** (70%)[e]	**4fH** (74%)[f]	**4gH** (73%)[e]
Z-Glycine, **3U**	**4aU** (73%)[g]	**4bU** (80%)[e]	**4cU** (78%)[f]	**4dU** (70%)[g]	**4eU** (65%)[g]	**4fU** (74%)[f]	**4gU** (71%)[f]
Z-L-Proline, **3V**	**4aV** (70%)[d]	**4bV** (74%)[d]	**4cV** (71%)[e]	**4dV** (75%)[e]	**4eV** (70%)[f]	**4fV** (69%)[f]	**4gV** (68%)[g]
Z-L-Valine, **3W**	**4aW** (72%)[d]	**4bW** (71%)[d]	**4cW** (74%)[f]	**4dW** (78%)[g]	**4eW** (71%)[f]	**4fW** (71%)[g]	**4gW** (65%)[g]

[a]Amines **1**: 0.6 M in $CHCl_3$, yield of amide **4** after purification. [b]Time for reaction completion (TRC) after the addition of R^3COOH: 2 h. [c]TRC after the addition of R^3COOH: 3 h. [d]TRC after the addition of R^3COOH: 4 h. [e]TRC after the addition of R^3COOH: 6 h. [f]TRC after the addition of R^3COOH: 8 h. [g]TRC after the addition of R^3COOH: 10 h. [h]TRC after the addition of R^3COOH: 16 h. [i]TRC after the addition of R^3COOH: 24 h.

Scheme 4. Possible Mechanism for the Sulfinyl/Carbonyl Exchange



prop-2-enesulfinyl amide **5ac**, *i*-PrOH with pivalic acid **3I** slow formation of isopropyl sulfinic ester **9b** and pyrrolidine is observed. In the presence of 1 equiv of water the yield in **4aA** for reaction **3A** + **5ac** drops to 40%.

At this stage of our studies we cannot exclude alternative mechanisms. One of them could be the formation of carboxylic anhydrides $(R^3CO)_2O$ resulting, for instance, from the reaction of sulfinyl carboxylates **8** with the carboxylic acid **3**. At 20 °C, 3-phenylpropionic acid anhydride reacts with pyrrolidine to give **3A** + **4aA**. We cannot exclude an intramolecular 1,3-transfer of the amino moiety in intermediate **7** onto its carbonyl group. If this mechanism should prevail it implies that the amino moiety of **7** can exchange with external amines. Without the amine, acid **3A** did not react with **2c** (1 equiv) at 20 °C. When Et_3N (1 equiv) was added to this mixture, sulfinyl carboxylate **8Ac** formed together with products of decomposition[10] of **2c**. Then the addition of **1a** (1 equiv) generated sulfinylamide **5ac** and acid **3A**. After this mixture was heated to 70 °C, amide **4aA** formed in 62% yield, only. This procedure is lower yielding than in the case of first generating the sulfinylamide.

In summary, an efficient and mild method has been developed for the one-pot, direct amidification of carboxylic acids that is applicable to primary and secondary amines, including the *tert*-butyl ester of α-amino acids. Aliphatic and aromatic carboxylic acids bearing unprotected alcohol, phenol, or ketone moieties can be used, including pivalic acid and benzylcarbamates of α-amino acids. Protected dipeptides have been obtained without α-epimerization of the carboxamides.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, spectra data, characterization data, and copies of ^1H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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